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Effect of hydrostatic pressure on the exchange interactions in a ferromagnetic spinel $CdCr_2Se_4$

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We have used electron paramagnetic resonance at hydrostatic pressures up to 8 GPa to study the pressure dependence of the nearest-neighbor and more-distant-neighbor exchange constants, J and K, in single-crystal samples of the ferromagnetic spinel $CdCr_2Se_4$. K is initially antiferromagnetic but changes sign near 5 GPa and increases rapidly at higher pressure. J remains ferromagnetic but decreases rapidly with pressure until at 8 GPA the total exchange contribution of the near neighbors becomes comparable to that of more-distant neighbors. We find that the lattice-constant dependence of J and K is much stronger than in the mixed-composition system $CdCr_2(Se_{1-x}S_x)_4$ studied by Wojtowicz, Baltzer, and Robbins. The pressure dependence of the EPR linewidth above T_c is found to scale with the reduced temperature $(T-T_c)/T_c$ but with a change in slope at high temperatures that we attribute to changes in the phonon spectrum.

I. INTRODUCTION

$CdCr_2Se_4$ is a ferromagnetic semiconductor with a Curie temperature T_C of 130 K.[1-4] Although the optical, electrical, and magnetic properties of $CdCr_2Se_4$ and other chromium chalcogenide spinels have been extensively studied since the early 1960's, these materials are still actively studied because of possible technological applications.[5]

In $CdCr_2Se_4$, a normal cubic spinel, the diamagnetic Cd^{2+} ions, and the magnetic Cr^{3+} ions, respectively, occupy the tetrahedral A sites and the octahedral B sites in an approximately face-centered-cubic lattice of Se^{2+} ions, as illustrated in Fig. 1.[6]

The magnetism of $CdCr_2Se_4$ results from superexchange interactions[7-9] between Cr^{3+} ions via intermediate Se^{2-}. The net nearest-neighbor exchange interaction J is ferromagnetic due to a 90° superexchange which dominates the antiferromagnetic direct exchange. But to explain the magnetic properties of these spinels, one must also consider the superexchange with more-distant neighbors. The strength (and sign) of the interaction with these more-distant neighbors varies widely.[10] In order to reduce the number of parameters, Baltzer *et al.*[1] have introduced a single antiferromagnetic effective exchange constant K for 30 more-distant neighbors. The magnetism of the spinels can then be understood in terms of the competition between J and K.

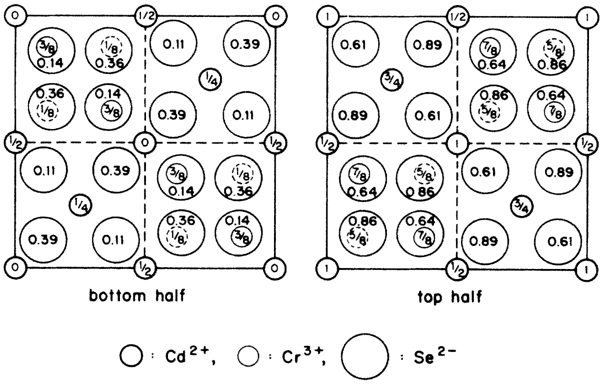

FIG. 1. Projections on a cube face of atoms in the normal spinel lattice of $CdCr_2Se_4$ with crystallographic u parameter 0.390. The numbers show the height of projected atoms above the projection plane.

In this paper we study the variation of J and K with pressure. Using electron paramagnetic resonance (EPR) we have determined the Curie temperature T_C and the paramagnetic Curie temperature Θ of single-crystal $CdCr_2Se_4$ under hydrostatic pressures up to 8 GPa. From these data we extract values for J and K using the method of Baltzer *et al.*[1] and compare our results with J and K for the system $CdCr_2(Se_{1-x}S_x)_4$.[11] In this mixed-composition system, substitution of the smaller S^{2+} ion for Se^{2+} reduces the lattice constant due to the shorter bond length and is therefore equivalent in some sense to applying pressure. In the last section of the paper we discuss the effect of pressure on the EPR linewidth.

II. EXPERIMENTAL

The EPR measurements were made using a Varian V-4500 100-kHz modulation spectrometer. Pressure was applied by placing the sample in a gasketed diamond-anvil cell. A large opening in the pressure cell permitted the X-band waveguide to pass through it and enclose the diamond anvils and gasketed sample. No resonant cavity was needed since the length of the gasket was adjusted to make it self-resonant at the desired frequency. A typical gasket 12.6 mm long by 7.1 mm wide by 0.20 mm thick resonated at 8.59 GHz with a Q of 700.

The single-crystal $CdCr_2Se_4$ that we studied was supplied by H. L. Pinch (RCA Laboratories, Princeton, New Jersey) and was grown by vapor phase transport. A single crystal was cut and polished into a small roughly circular disk (0.1 mm in diatmeter by 0.06 mm thick). The crystallographic orientation was random. The disk was placed in a 0.15-mm-diam hole in the gasket resonator, together with a ruby chip for pressure measurement and a mixture of 4 parts methanol to 1 part ethanol for pressure transmission. The gasket material was Be-Cu (Berylco 25) hardened by heat treatment at 320 °C for two hours and precompressed from a thickness of 0.20 mm to about 0.12 mm between diamond anvils with 0.6-mm-diam faces.

High pressure was generated by pushing one anvil down with a piston driven by a differential screw which could be hand rotated from the top of the dewar. The pressure was measured using the ruby fluorescence method.[12] This permitted the pressure to be changed and calibrated while the diamond-anvil cell was at low temperature. The temperature was electronically controlled with exchange gas and a constantan wire heater attached to the cell body. It was measured with a platinum resistor thermometer mounted on the cell body as near to the sample as possible. We have described the system elsewhere.[13]

III. RESULTS AND DISCUSSION

A. Effect of pressure on the transition temperatures

The room-temperature electron-spin-resonance spectrum of our $CdCr_2Se_4$ samples consists of a single isotropic line at $g = 1.998 \pm 0.001$ with a linewidth (peak-to-peak absorption derivative) $\Delta H_{pp} = 102 \pm 3$ Oe, in good agreement with previous results.[14] The line shape is Lorentzian, except near T_C.

In order to determine the paramagnetic Curie-Weiss temperature Θ, we plotted against temperature the reciprocal of the integrated intensity $\Delta H_{pp}^2 h$, where h is the peak-to-peak height normalized to a reference sample.[15] Θ was obtained by extrapolating the linear high-temperature region (200—300 K) of the plot to zero. This procedure is valid if there are no line-shape changes and data can be obtained over a wide enough T range. The temperature variation of the EPR spectrum was measured at each pressure setting to obtain $\Theta(P)$.

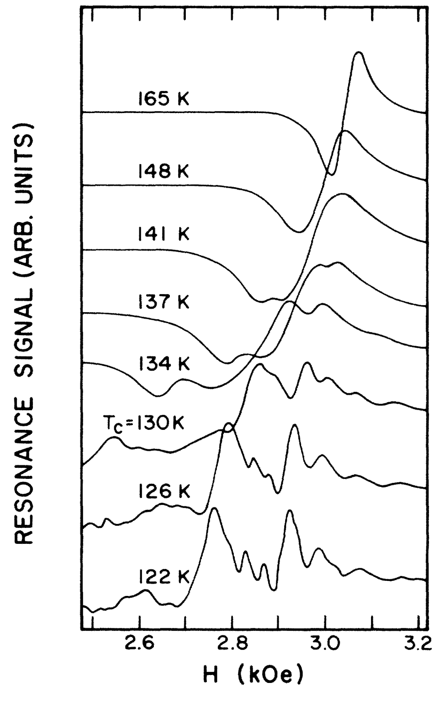

FIG. 2. Temperature dependence of the EPR spectrum of $CdCr_2Se_4$ in the diamond-anvil cell at ambient pressure. The Curie temperature is 130 K.

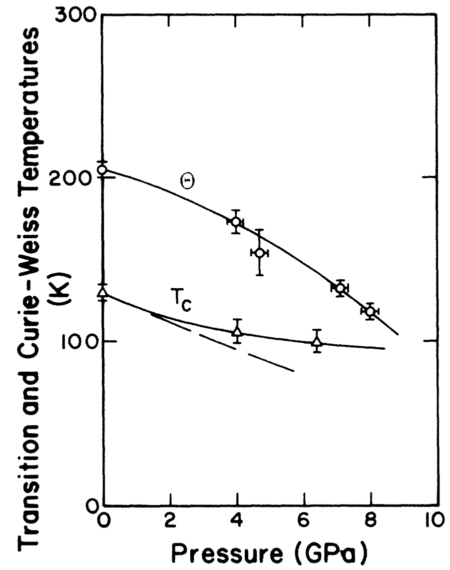

FIG. 3. Paramagnetic Curie temperature Θ and Curie temperature T_C versus pressure for $CdCr_2Se_4$. Dashed line is the initial slope $dT_C/dP = -8.2$ K/GPa obtained by Srivastava (Ref. 18) for pressures up to 1 GPa.

It is difficult to accurately determine T_C from the EPR signal, since there is no sharp change in the signal marking the onset of magnetic order. Near T_C the resonance shifts rapidly to lower field due to demagnetization and the spectrum is complicated by the appearance of magnetostatic modes.[16,17] Typical spectra are shown in Fig. 2. We estimated T_C as the center temperature of the 10—15-deg range where the changes in the spectrum and the resonant field shift become pronounced.

Figure 3 shows the variation with pressure of Θ and T_C. The errors in Θ come from scatter in the integrated intensity, which we could only obtain to 10%, and from pressure variation. In our system, thermal contraction causes the pressure to vary with temperature. Although the pressure can be changed at low temperatures to compensate, it is not easy to adjust the pressure as a totally independent variable. The data in Fig. 3 are an average of data taken over a small pressure range.

The initial slope of the pressure dependence of T_C in Fig. 3 agrees with the value − 8.2 K/GPa obtained by Srivastava[18] from mutual inductance measurements at pressures up to 1 GPa. The ambient pressure Θ agrees well with $\Theta = 204$ K obtained by Baltzer *et al.*[1] and $\Theta = 210$ K obtained by Menyuk *et al.*[3] from static susceptibility measurements. We see in Fig. 3 that Θ and T_C both decrease with pressure but that the change in Θ is more pronounced.

B. Effect of pressure on the exchange interactions

Baltzer *et al.*[1] have developed a model to explain the ferromagnetism of the spinels on the basis of a Heisenberg spin Hamiltonian of the form

$$\mathscr{H} = -g\mu H_z \sum_i S_{iz} - 2J\sum_{i,j} \mathbf{S}_i\cdot\mathbf{S}_j - 2K\sum_{i,k} \mathbf{S}_i\cdot\mathbf{S}_k \ . \tag{1}$$

The first term is the Zeeman energy in an external field H_z. The second term includes six nearest-neighbor pair interactions with a single exchange parameter J, and the final term includes more-distant pair interactions which are assumed to have identical strength K. They considered 30 more-distant interactions including 12 second-nearest neighbors at a distance $(a/4)6^{1/2}$, 6 third-nearest neighbors at a distance $(a/4)8^{1/2}$, and 12 fourth-nearest neighbors at a distance $(a/4)10^{1/2}$ (see Fig. 1). These interactions occur by the same type of extended superexchange path, $Cr^{3+}-Se^{2-}-Cd^{2+}-Se^{2-}-Cr^{3+}$. Six third-nearest-neighbor interactions with a different path, $Cr^{3+}-Se^{2-}-Cr^{3+}-Se^{2-}-Cr^{3+}$, are neglected (see Fig. 6 of Ref. 1).

Although this approximation has been criticized in terms of the relation between the symmetry of the electron orbitals and the superexchange interaction,[10] it greatly simplifies the problem by reducing the number of independent variables and makes it possible to qualitatively understand $CdCr_2Se_4$. In this paper our purpose is to find how pressure changes the size of this effective or average K.

We can use our data on the pressure dependence of Θ and T_C to determine how J and K are affected by pressure. Θ and T_C can both be obtained from the susceptibility calculated using the Hamiltonian of Eq. (1). Θ is simply the leading term in an expansion of the inverse susceptibility in powers of $1/T$, and is then linear in J and K:[1]

$$\Theta = \tfrac{2}{3}S(S+1)[zJ+yK]/k \ , \tag{2}$$

where S is the spin, k is Boltzmann's constant, z is the number of nearest neighbors, and y is the number of distant neighbors. In the case of $CdCr_2Se_4$, $S=\frac{3}{2}$, $z=6$, and $y=30$.

T_C is more difficult to evaluate. When $K=0$, T_C can be evaluated by numerically evaluating the first n terms in the series expansion of susceptibility in $1/T$ and extrapolating to large n.[19,1] For $CdCr_2Se_4$, $kT_c/J=9.8\pm0.1$, while for $K=0$ in Eq. (2), $k\Theta/J=15$ and $\Theta/T_C=1.53$. In our measurements Θ/T_C varies between 1.64 and 1.24. Thus, the spin statistics $(S=\frac{3}{2})$ and lattice structure alone[19] are not adequate to explain the data and more-distant exchange interactions $(K\neq0)$ must be considered. Baltzer *et al.*[1] have computed T_C as a function of J and K using a two-particle cluster approximation. They give a graph of Θ/T_C versus K/J, which when used with Eq. (2), allows us to determine K and J. Figure 4 gives our results for J and K as functions of pressure that we obtained from the smoothed curves in Fig. 3. The error bars assume errors of ±3 K for both Θ and T_C. The positive ferromagnetic nearest-neighbor exchange decreases rapidly with pressure and extrapolates to zero near 9 GPa. On the other hand, the initially antiferromagnetic K has a shallow minimum at 2 GPa and becomes ferromagnetic near 5 GPa. At 8 GPa the total contribution of distant-neighbor interactions yK equals that of nearest-neighbor interactions zJ.

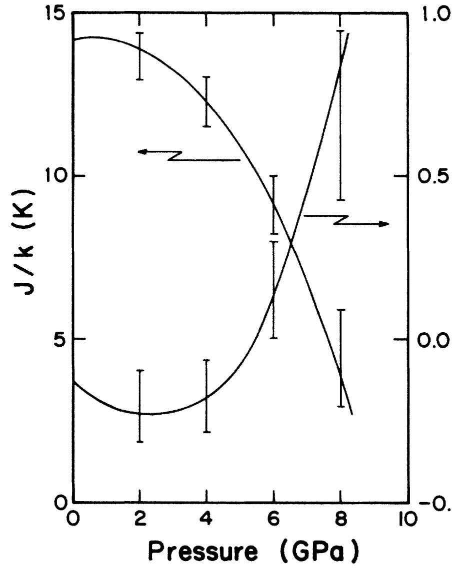

FIG. 4. Pressure dependence of the nearest-neighbor and more-distant-neighbor exchange interaction strengths, J and K, in $CdCr_2Se_4$. Positive values of J and K are ferromagnetic.

Partial ligand substitution with different sized ions is a commonly used technique to controllably vary the lattice parameter and thus study the effect of separation on ion interactions. Wojtowicz *et al.*[11] have studied the magnetic and crystallographic properties of the mixed-compositional system $CdCr_2(Se_{1-x}S_x)_4$, where substitution of the smaller S^{2-} ion for Se^{2-} compresses the lattice constant. Their results for Θ and T_C are given in Fig. 5.

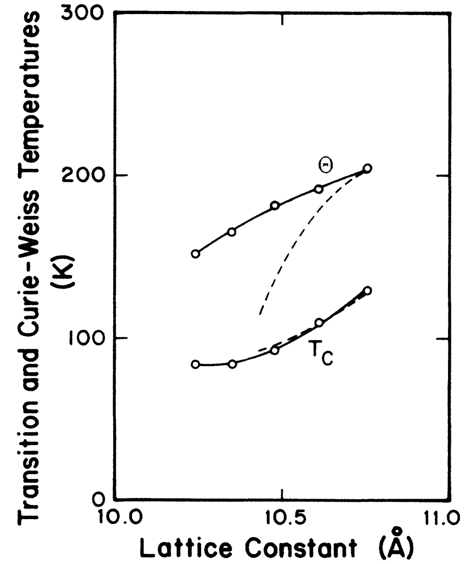

FIG. 5. Paramagnetic Curie temperature Θ and Curie temperature T_C versus lattice constant a. ——, $CdCr_2(Se_{1-x}S_x)_4$ (Ref. 11); — — —, hydrostatic pressure on $CdCr_2Se_4$ (our results).

In order to compare the effects of chemical or lattice pressure with hydrostatic pressure, we need compressional data to convert applied pressure to a change in lattice constant. Since at present there are no compression data for $CdCr_2Se_3$ up to 8 GPa, we estimate the pressure dependence of the lattice constant at room temperature with the Birch-Murnaghan equation of state[20,21]

$$P=\tfrac{3}{2}B_0[(V_0/V)^{7/3}-(V_0/V)^{5/3}] \ , \tag{3}$$

where P is pressure, V_0/V is volume ratio, and B_0 is the initial bulk modulus. Low-pressure compressibility measurements have been made on single-crystal $CdCr_2Se_4$ by Batlogg *et al.*[22,23] using a strain gauge up to 0.5 GPa. Their value of $1.3\times10^{-6}\ \mathrm{bar}^{-1}$ yields $B_0=77$ GPa.

In Fig. 5 we translate our data on the pressure dependence of Θ and T_C (Fig. 2) to lattice-constant dependence using Eq. (3). In Fig. 6 we make a similar transformation of our smooth curves for J and K given in Fig. 3 and compare them with Wojtowicz's data for the compositional system. We remark that Brown[24] has used a different fitting procedure for J and K for the mixed-composition system. It assumes the same model but finds somewhat different values for J and especially K. It is not applicable to our pressure data.

The pressure and substitutional methods give quantitatively very different results. This is not surprising. In the first place, when S^{2-} is substituted for Se^{2-}, the difference in covalency of the two ions changes the nature of the bond, that is, the bonding with S^{2-} is more ionic than that with Se^{2-}. This is especially important for magnetic interactions where the 90° superexchange interaction passes through the Se^{2-} ions.

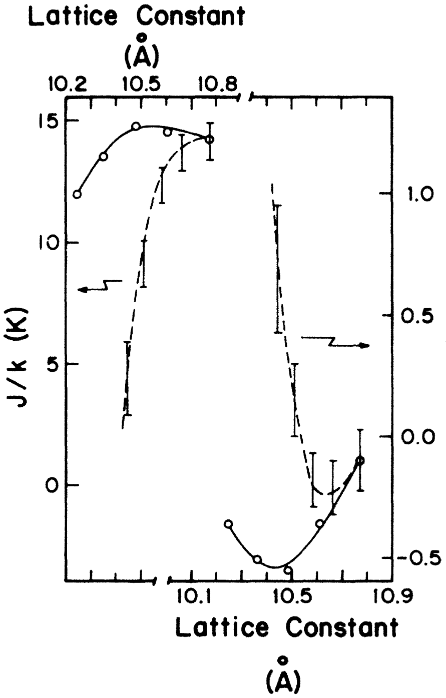

FIG. 6. Nearest-neighbor and more-distant-neighbor exchange interaction strengths, J and K, versus lattice constant a. ——, $CdCr_2(Se_{1-x}S_x)_4$ (Ref. 11); – – –, hydrostatic pressure on $CdCr_2Se_4$ (our results).

Batlogg *et al.*[25] have compared the change in band gap of SmSe when the lattice constant is compressed by hydrostatic pressure and by lattice pressure ($SmSe_{1-x}S_x$). They found that hydrostatic pressure induces a much more rapid decrease in band gap than lattice pressure, which they likewise attributed to the change in covalency with anion substitution.

A second less important reason for the difference in response to the two types of pressure is that the local lattice distortion is probably different for the two cases. This is important because the 90° superexchange, while dependent on the separation of the interacting ions, is also very sensitive to deviation of the bond angle from 90°. For $CdCr_2Se_4$ the crystallographic u parameter, 0.390, deviates from the ideal value 0.375 for close packed Se^{2-} ions. Because of this, the nearest-neighbor $Cr^{3+}-Se^{2-}-Cr^{3+}$ bond angle is 97° rather than 90°. Wojtowicz *et al.* measured u in the mixed-composition system and found only slight variation with S^{2-} content, so the bond angle remains unchanged. For hydrostatic pressure we expect u to change, since Göbel[26] observed that when $CdCr_2Se_4$ is cooled u increases, reaching 0.392 at 77 K. Assuming that the effect of hydrostatic pressure resembles thermal contraction, the 97° bond angle should increase with pressure.

In addition to the effect of pressure on the superexchange interaction, the possibility of contribution of direct exchange interaction between Cr^{3+} ions will have to be considered at high pressures, because this interaction is usually weak but sensitive to the atomic distance.

Finally, it should be noted that our results for $CdCr_2Se_4$ show strong contrast with insulating materials such as several garnets, ferrites, and europium chalcogenides whose Curie temperatures increase with increasing pressure, and in which Bloch[27] has found that the exchange interactions vary as the $-\frac{10}{3}$ power of the volume ($d\ln J/d\ln V=-\frac{10}{3}$). This power law is not observed in metals[28] and its failure to hold in $CdCr_2Se_4$ may reflect d banding, so that there may be an extensive direct d-d exchange.[29] This view is consistent with claims of mixed-valence behavior in $CdCr_2Se_4$.[30]

C. Effect of pressure on the EPR linewidth

Figure 7(a) gives the temperature dependence of the EPR linewidth of our sample at ambient and at 6-GPa pressure. For comparison we show data taken by Kötzler and von Philipsborn[31] on a polished sphere of $CdCr_2Se_4$. Their data agree well with similar measurements by Berzhansky *et al.*[32] Our data show excess broadening at all temperatures, which we attribute to a slight deviation from stoichiometry in our sample. The broadening mechanism is either free carriers or disproportionation of the Cr^{3+} to yield Cr^{2+} and Cr^{4+} ions.[33] It has previously been found that the EPR linewidth in $CdCr_2Se_4$ and related spinels is affected by vacuum annealing, annealing in a Se atmosphere, or doping with Ag (which substitutes for Cd^{2+} as Ag^{+}).[34–36]

The solid line in Fig. 7(a) is a fit of Kötzler's data to the expression used by Berzhansky for a Lorentzian line shape:[32]

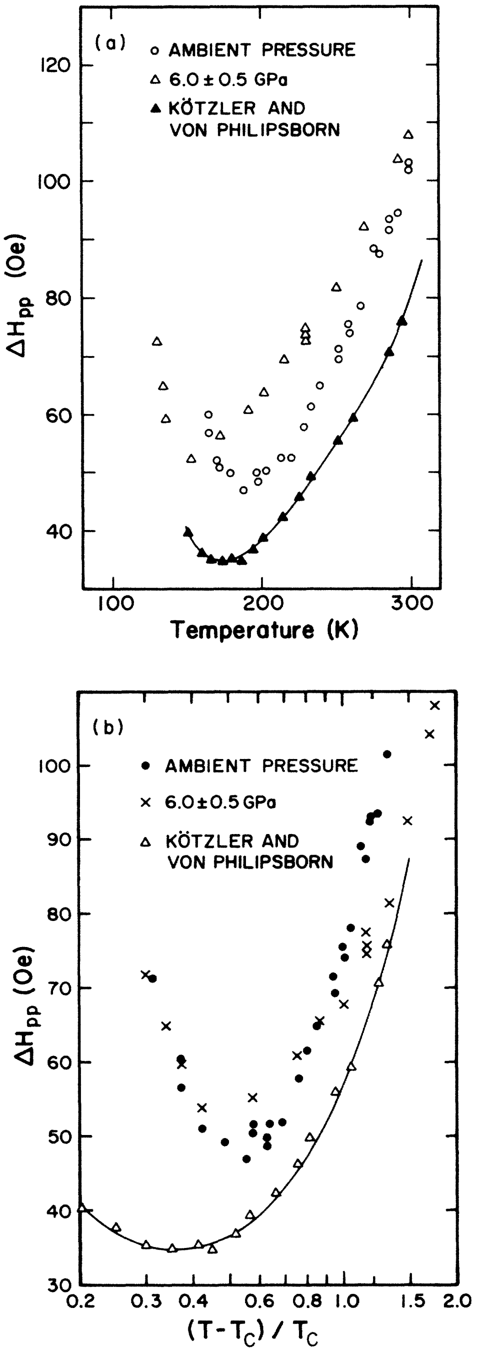

FIG. 7. (a) Temperature dependence of derivative peak-to-peak EPR linewidth of $CdCr_2Se_4$ at ambient pressure and 6.0 GPa compared to the data of Kötzler and von Philipsborn (Ref. 31). Solid line is fit to Eq. (5). (b) Linewidth data plotted versus reduced temperature, $\tau=(T-T_C)/T_C$. For ambient pressure $T_C=130$ K and for 6 GPa, $T_C=107$ K.

$$\Delta H_{pp}=\frac{2}{\sqrt{3}}[\Gamma_{sl}+\Gamma_d(0)+\Gamma_d(H)] \quad (4)$$

$$=\frac{2}{\sqrt{3}}(A\tau^{\gamma}+B\tau^{-3\gamma/4}-C\tau^{-(\gamma+3p/2)}) \ , \quad (5)$$

where $\tau=(T-T_C)/T_C$, the critical exponent for the susceptibility $\gamma=1.30\approx\frac{4}{3}$, and the critical exponent for spin diffusion $\rho=0.30\approx\frac{1}{3}$.[37,38] Γ_{sl} is the broadening due to spin-lattice relaxation which increases monotonically with temperature.[39] The peak in the linewidth near T_C is due to dipolar spin-spin interaction $\Gamma_d(0)$, which has a magnetic field dependence $\Gamma_d(H)$ due to spin diffusion.[40] For *X*-band measurements $\Gamma_d(0)$ and $\Gamma_d(H)$ almost cancel, leaving a small residual critical peak.

Our data cannot be fit with Eq. (5) due to the extra broadening which enhances the size of the critical peak. However, the important point is that Eq. (5) predicts that ΔH_{pp} should scale with T_C. We take into account the shift in T_C with pressure by replotting ΔH_{pp} as a function of τ in Fig. 7(b). In order to make the data for the two pressures coincide at low *T*, we have used $T_C=107$ K for the 6-GPa data, which is in good agreement with $T_C=102$ K from Fig. 3. The shift in T_C accounts for the entire variation in linewidth with pressure except for a decrease in $d\Delta H_{pp}/dT$ for large *T* and a possible increase in the minimum linewidth near $\tau=0.5$. These changes are easily understood; Huber and Seehra[39] attribute the high-temperature linewidth Γ_{sl} to phonon modulation of the crystalline field. They argue that single-phonon processes are much more important in magnetically concentrated systems than for the single-ion case because the spectral width of the spin-spin correlation functions allows a broad band of phonons to produce spin-lattice relaxation. Then the change in slope (and minimum linewidth) with pressure is the result of the change in the phonon spectrum as the lattice is stiffened by compression.

The room-temperature slope of our ambient-pressure linewidth, 0.83 Oe/K, agrees well with the value 0.86 Oe/K Berzansky *et al.*[14,41] obtained over the temperature range 400–600 K. At 6 GPa this slope is 0.59 Oe/K. The scatter in our data, which comes from our difficulty in keeping the pressure constant as *T* changes, and the reduced signal-to-noise prevents us from obtaining more quantitative results.

IV. CONCLUSION

Using a diamond-anvil electron-resonance apparatus, we have measured the pressure dependence of the Curie-Weiss temperature Θ and the ferromagnetic transition temperature T_C of the spinel $CdCr_2Se_2$ for hydrostatic pressures up to 8 GPa. Our results for T_C agree with Srivastava's earlier low-pressure (1 GPa) measurements.[18] We have analyzed our data using a simplified Heisenberg Hamiltonian in which 30 distant-neighbor exchange constants are assumed to have the same value *K*.[1] This analysis gives the pressure dependences of *K* and *J*, the nearest-neighbor exchange constant. *J* decreases rapidly with pressure, extrapolating to zero at 9 GPa. *K* is initially negative (antiferromagnetic) but changes sign near 5 GPa and then increases rapidly. At 8 GPa the total distant-neighbor exchange equals that of the six nearest neighbors.

We have compared the effects of hydrostatic pressure and lattice pressure on Θ and T_C by comparing our data with that of Wojtowicz *et al.*[11] on the system $CdCr_2(Se_{1-x}S_x)_4$, where substitution of the smaller S^{2-}

ion for Se^{2-} "compresses" the lattice constant. We find that the two types of lattice compression have widely different effects on J and K, which we attribute largely to the change in the degree of covalency of the bond when S^{2-} substitutes for Se^{2-}.

We find that to first order the effect of pressure on the temperature dependence of the electron-resonance linewidth can be explained by scaling the linewidth as $(T-T_C)/T_C$. This is to be expected since the EPR broadening is a critical phenomenon and the pressure-induced changes in J and K are reflected in T_C. At temperatures well above T_C, we see a reduced linewidth under pressure that we attribute to a change in the phonon spectrum.

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